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FINAL REPORT

GELLING OF LIQUID HYDROGEN

by

Herbert Karl Luke, C. Dana McKinney, Richard Pheasant, and William B. Tarpley

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

July 31, 1964

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FOREWORD

TECHNIDYNE INCORPORATED* - THE MARQUARDT CORPORATION

This program was undertaken as an effort of the above team with Technidyne Incorporated as the prime contractor. Technidyne was responsible for carrying out virtually all of the laboratory work in its own facilities.

The Marquardt Corporation (ASTRO Division) was the subcontractor member of the team, providing thermochemical assistance, gel-usage criteria, guidance in the handling properties of liquid hydrogen, and engineering support in the design of the liquid hydrogen cryostat.

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ABSTRACT

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Gel technology developed mainly for conventional liquid propellants has been applied to liquid hydrogen (LH₂). The low boiling point (20.3°K), low density (0.07 g/cm³) and low degree of association of LH₂ posed unique problems in gellant selection. Solubility factors tended to limit the investigations to gellants of the particulate type, including those created in situ.

Particle spacing considerations for the finest initially available particulate gellants (such as carbon black or silica) indicated that on the order of 40 w/o gellant would be required, because of the high density ratio of gellant to LH₂. Hence, new gellants were required.

The most effective commercially available particulate gellant, pyrogenic silica (in the finest particle size, 7 mμ) formed gels in LH₂ at a loading of 35-37 w/o, or 1.8-1.9 v/o (i.e., slightly less than predicted). Such a concentration of inert additive would lead to serious decrement in propulsion performance. Nevertheless, the gel was useful for flow and certain other property simulation. The rheological properties of several such gels, at 20°K, were comparable to those of liquids gelled at ambient temperatures. The yield stresses (a measure of consistency) were in the 500-1000 dynes/cm² range which appears suitable for liquid propellants.

A search for high-energy, low-density solid fuels which might be preparable in the ultrafine particle size requisite for gelation revealed, for example, lithium borohydride (LiBH₄, 0.66 g/cm³). Calculations, without optimization, have shown that, even with as much as 20 w/o (2.56 v/o) of LiBH₄ loading, LH₂ performance degradation with LOX would amount to only 4.5 percent, or with LF₂ only 2.5 percent.

Preliminary preparations of fuel-gellants were made for screening purposes, albeit the particle sizes were larger than optimal. LH₂ gels were made as follows: lithium borohydride 67 w/o (17 v/o), and lithium aluminum hydride 86 w/o (32 v/o). Aluminum flake gave some evidence of gel formation at 73 w/o (7.5 v/o). Other candidate fuel-gellants which were briefly examined and appear promising include boron, boranes, methane (in situ), hydrazine, and certain light metal hydrides. The ultimate choice depends on such factors as low density, high energy contribution, and ease of preparation of particles in sizes below 50 mμ.

Several of the above LH₂ gels showed reduced evaporation rates (25 percent of that of neat LH₂), resistance to vibratory acceleration (3 G, 120 cps) and shock acceleration (14 G).

In this work a laboratory cryostat was used which provided three features not generally included in LH₂ equipment -- full-depth visual observability, high-shear mixing, and viscometry.



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I. INTRODUCTION

Thixotropically gelled liquid rocket propellants (thixotropes), which behave as solids under the low stresses of storage and bulk transportation, but transiently liquefy during pumping or pressurized flow, have been the subject of increasing scientific investigation over the last 7 years.

Of special pertinency to the task of gelling liquid hydrogen, the Technidyne group gelled liquid nitrogen (the first reported cryogenic gel) several years ago, and observed that the evaporation rate was reduced more than three-fold (Figure 1). Other liquefied gases such as ammonia, methyl chloride, Freons, and low-boiling hydrocarbons had been gelled at that time. It was postulated that evaporation should be reduced even more with larger scale tankage.

Reduced evaporation losses are particularly beneficial in gelled cryogenic propellants. Performance advantages of gelled liquid propellants in general appear to include damping of sloshing or of resonant vibration, and retention of shape and position (e.g., as in a weightless environment). The tensile properties of gels should facilitate their transfer.

Other advantages are in safety and damage control. Gelled liquids, on spilling, remain in a pile rather than flowing, and vaporize much more slowly than ungelled liquids. They may be removed by solid-materials-handling equipment. In the event that a tank ruptures or is penetrated by a flying object, leakage is minimized and shock effects are damped.

This exploratory formulation study in the gelling of liquid hydrogen was aimed at realizing all of the general advantages of thixotropic propellants, as well as showing reduced evaporation losses. Looking beyond the scope of this task, stabilized slurry gels in liquid hydrogen may offer a means of increasing the propellant density of hydrogen with concomitant improvement in over-all system performance.

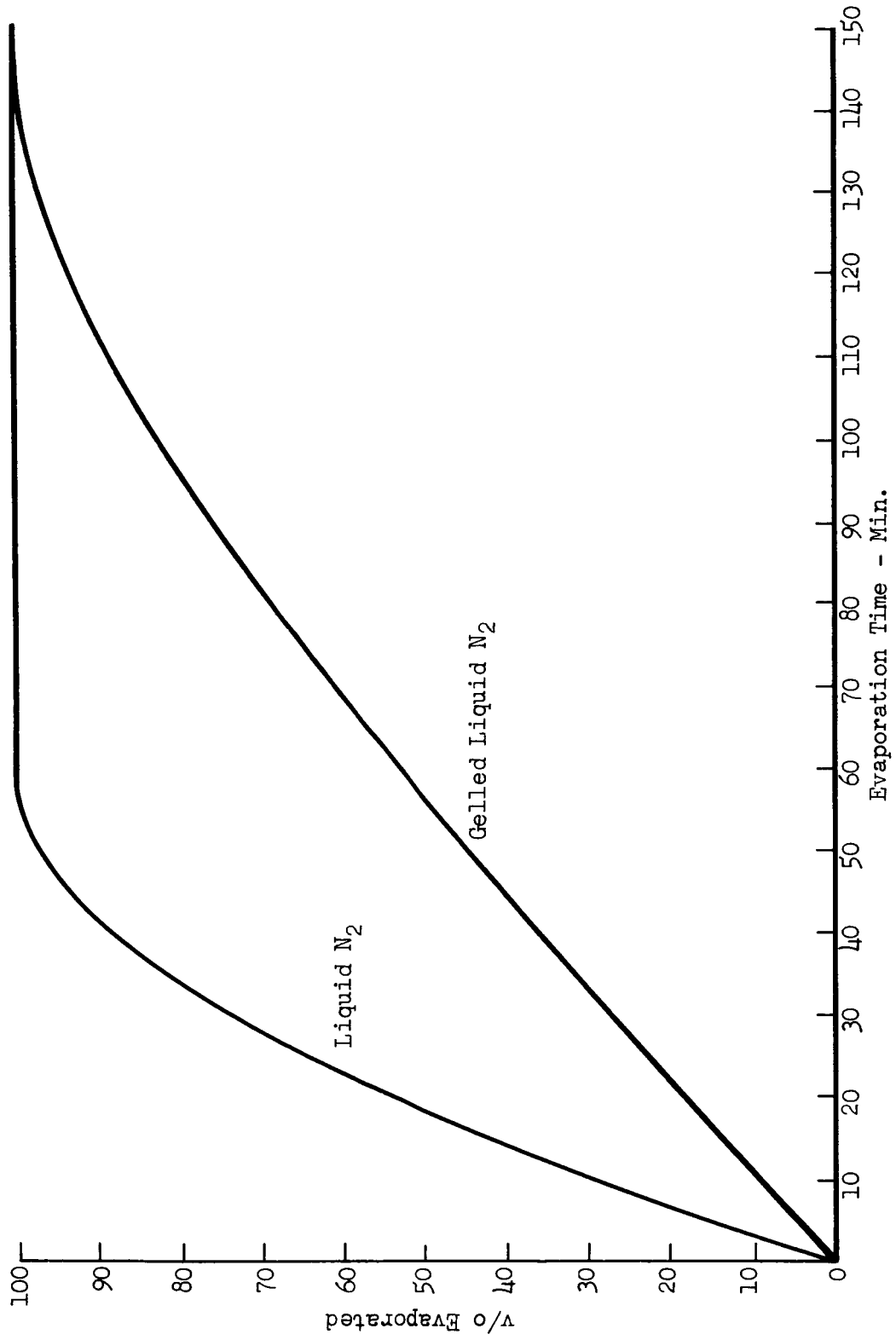


Figure 1
EVAPORATION RATE OF LIQUID NITROGEN

II. THEORETICAL CONSIDERATIONS

As a liquid, hydrogen is unique. It is weakly associated and has a very small spread between freezing and boiling points. Its density and viscosity are also extremely low. In general, its physical properties seem to be intermediate between those of the inert gases and those of other cryogenics. It is reported to be incapable of dissolving any substance with the exception of helium.

No evidence has been reported of the existence of liquid hydrogen molecules larger than H_2 . Furthermore, the Trouton constant of 10.5 suggests an unusually low degree of association (see Table I). This is undoubtedly a factor in the low solvent power of liquid hydrogen.

The dielectric constant of normal liquid hydrogen at its boiling point is 1.23, indicating very low polarity and little or no ionization.

These properties, combined with the low-temperature operating range, present challenging problems in gel preparation and characterization. The static and rheological characteristics of any gelled propellant require detailed definition using the best viscometric techniques, in order to avoid anomalous results when relating to end-use studies. This is of paramount importance in working in the cryogenic temperature range, and specialized adaptations of instrumentation were required.

As a result of earlier work in this laboratory (1)* gellants have been divided into "swellable" and particulate categories. The class termed "swellable", consisting of long-chain macromolecules with lyophilic substituent groups, owes its effectiveness to the affinity of these groups for, and partial solubility in, the liquid being gelled. No such solubility behavior has been found with liquid hydrogen, and it appears doubtful that swellable gellants will prove useful in this application. "Particulate" gellants are completely insoluble ultrafine particles, which gel through a mechanism of interparticulate forces, often influenced by surface chemistry. To the extent that the effect of low dielectric constant on gelling at 20°K may be similar to its effect at 20°C, one would expect the high-surface type of particulate gellant to be indicated, and the polymeric type to be contra-indicated.

The minimum quantity of a particulate gellant was shown to be a function of particle size, particle density, and liquid density. There must also be the proper interaction between the liquid and the surface chemistry of the particle for the gellant to be effective. For example, colloidal silica, which is a good gellant for almost all non-polar and moderately polar liquids, will not gel highly polar liquids, such as water, without the addition of a third component to alter the interfacial tension and surface charges (1) (2).

* Numbers in parentheses designate references listed at end of report.

Table I

ABBREVIATED TABLE OF PROPERTIES OF CERTAIN LIQUIDS

<u>Liquid</u>	<u>Liquid Density at b.p., g/ml</u>	<u>Heat of Vaporization at b.p., cal/mol</u>	<u>Boiling Point, °K</u>	<u>Trouton Constant</u>	<u>Thixotropically Gelled</u>
Hydrogen	0.07	214.8	20.3	10.5	With Particulate*
Helium	0.125	19.56	4.2	4.6	
Nitrogen	0.81	1322.0	77.4	17.1	With Particulate
Methane	0.424	1945.0	111.7	17.4	With Particulate
NH ₃	0.68	5576.0	239.8	23.3	With Particulate
H ₂ O	0.958	9735.0	373.16	28.3	With Particulate or Swellable

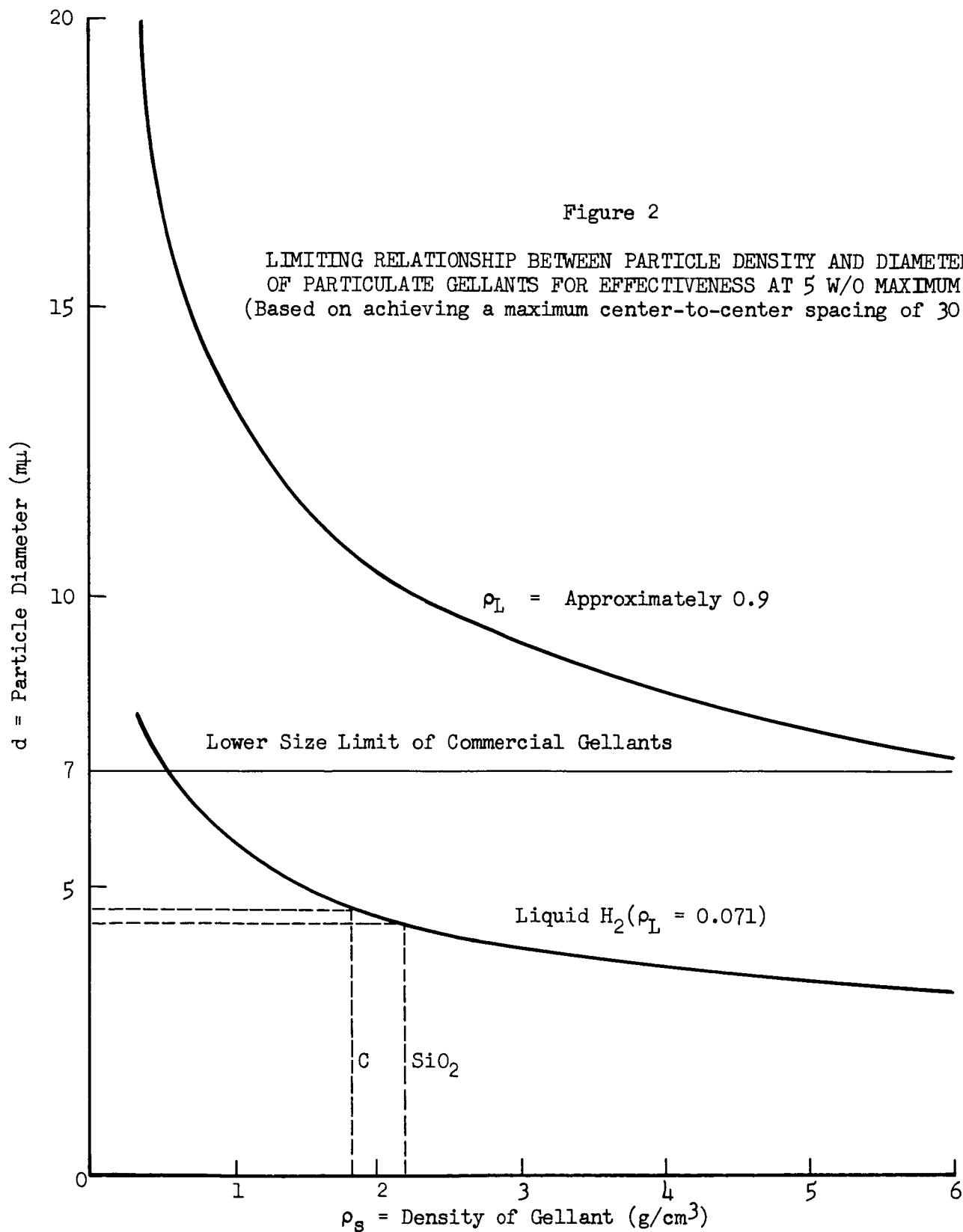
* As a result of this contract.

The search for gellants for hydrogen, therefore, has been targeted primarily toward insoluble submicron particles of low density, and with surface chemistry such that they exhibit an affinity for hydrogen. If possible, the gellant should also have fuel value, and fuels which are liquids or gases at ambient temperatures can be considered candidate gellants, since they will be solid at liquid hydrogen temperatures.

The density of liquid hydrogen (0.070 g/cm^3 at its boiling point) is lower by nearly a full order of magnitude than that of any other liquid fuel which has been gelled. An empirical relationship between particle size, particle density, and liquid density has been developed in our laboratory. Gellant particle spacing correlates via a family of curves plotting gellant density against particle size, with liquid density as the parameter. Figure 2 shows such a curve computed for liquid hydrogen and contrasted with a correlation of experimental data for a liquid of density approximately 0.9 g/cm^3 . Any particulate gellant of a size and density which falls below the appropriate liquid's curve is a candidate gellant if its surface characteristics permit affinity with the liquid.

For example, silica and carbon black, with densities of 2.2 and 1.8 respectively, are available in particle sizes in the neighborhood of $7 \text{ }\mu\text{m}$. These are adequate gellants for liquids of higher density, but would need to be prepared in a size range below 3.5 to $4.5 \text{ }\mu\text{m}$ to be effective in liquid hydrogen at 5 w/o gellant.

Alternately, if one accepts the present apparent lower size limit of commercially available materials, $7 \text{ }\mu\text{m}$, a density of about 0.6 would be the maximum for candidate liquid hydrogen gellants (which would function at 5 w/o or lower concentrations). A few materials exist in this density region, but not in the small size, e.g., lithium and some of its compounds, certain beryllium compounds, certain organics, and so forth. Higher concentrations than 5 w/o would be tolerable if the gellant contributed to the propulsion performance of hydrogen. It therefore appeared desirable to seek ultrafine particles of substances with very low densities, and preferably with some thermodynamic contribution to the I_{sp} .



III. GELLANT INVESTIGATIONS

A. Screening and Evaluation of Candidate Gellants

The foregoing theoretical considerations and analysis of the problems indicated that the gellants to be considered fell into roughly three categories, as follows:

Existing particulate gellants, many of which (save possibly carbon black) are non-energy-contributors.

Solid fuels.

Liquid and gaseous fuels.

In all cases it was recognized as expedient, and planned as a part of this program, to evaluate gellants as fully as possible in relatively easily handled simulant liquids. This would serve to narrow the selection for trial in liquid hydrogen. Normally, gellant screening and evaluation would be conducted using liquids with a range of polarities, from non-polar (e.g., hydrocarbons) through intermediate polarity (e.g., UDMH) and high polarity (e.g., hydrazine). In this case it was necessary only to use non-polar liquids, and to approach the simulation of other properties of hydrogen.

No suitable liquid is available which simulates all of the pertinent properties of liquid hydrogen (only liquid helium approaches it in density). However, there are some liquids with properties between those of hydrogen and those of liquids whose behavior with gellants has been studied extensively. Liquid nitrogen has intermediate physical properties and is cryogenic, and the lighter saturated hydrocarbons have some chemical similarity, with some intermediate physical properties. Both are non-polar, as is hydrogen, and are relatively poor solvents.

1. Effect of Hydrocarbon Density on Gellant Quantity

Investigations into the mechanism of gelling by particulate gellants had shown the calculated particle-to-particle spacing to have a maximum value for a given particulate gellant specimen. However, gellant surface chemistry and other factors play a role in the behavior of various types of gellant preparations (see Section II, above). This means that the required amount of a given gellant, used within a family of chemically related liquids, is approximately constant on a volume fraction basis for gels of comparable yield stress. If the density of the liquids within the family varies greatly, those of lower density will require relatively higher weight percentages of gellant.

Data pertinent to the liquid hydrogen gelation problem have been obtained and are shown in Table II. Normal heptane (density 0.684 g/cm^3) requires about 9 w/o of carbon black Type AB to form a gel with yield stress over 500 dynes/cm^2 . Liquid methane (density 0.415 g/cm^3), which has the highest hydrogen content of any hydrocarbon, was gelled at its boiling point (-161.5°C) as a simulant for liquid hydrogen. The gelation appeared to proceed normally and required 13.2 w/o of carbon black Type AB to attain a yield stress of 500 dynes/cm^2 . The increase in gellant quantity (in terms of w/o) needed for the lighter liquids supports the earlier observations of the relative constancy of interparticulate distance.

If one may assume that liquid methane and liquid hydrogen will interact similarly with gellants, the quantity of carbon black (Type AB) needed can be estimated. Extension of the above data to liquid hydrogen predicted that on the order of 45 w/o of acetylene black would be required to gel it. Later in this report it will be seen that LH_2 formed an incipient gel at 28 w/o, the maximum amount tried. Further reduction in particle size, and/or a lower-density gellant, would be needed for a satisfactory gel at an acceptably low weight percent.

2. Existing Particulate Gellants

Normal heptane ($\rho = 0.68 \text{ g/cm}^3$, b.p. = 98°C) and liquid nitrogen ($\rho = 0.81 \text{ g/cm}^3$, b.p. = -196°C) were used to examine the action of seven selected particulate gellants that had not been evaluated with these liquids heretofore.

All trial gellants were dried and outgassed by applying high vacuum ($<0.25 \text{ mm Hg}$) at elevated temperature and releasing the vacuum with dry nitrogen, repeated for a total of three times. These precautions were applied to remove adsorbed air and moisture. The gelling experiments were conducted in a dry box which was purged with dry nitrogen, and the motor for the mixer was driven by dry nitrogen instead of air, to prevent introduction of oxygen or moisture by accidental leakage.

The potential gellants used and the results obtained are listed in Table III. Heptane appeared to be gelled by the carbon black, and flake alumina, and possibly by pyrogenic alumina and titania. Thixotropic gels in liquid nitrogen, with significant yield stresses, were formed with acetylene black at 5.5 w/o, with a conductive furnace (carbon) black, at 8.5 w/o and with 7 μ silica at 4.6 w/o. The aluminas and titania, though in the proper particle size for gelling, settled out instead of dispersing, indicating that surface-active third components might be needed to assist in gel formation.

By measurement with a penetrometer, yield stresses were determined for the successful LN_2 gels, and are listed in the last column of Table III.

Table II
RELATIVE GELLANT* CONCENTRATIONS
FOR COMPARABLE GEL PROPERTIES

	Yield Stress d/cm^2	Liquid Density g/cm^3	Gellant Required	
			w/o	v/o
Heptane	550	0.684	9	3.4
Methane	500	0.415	13.2	3.2
LH ₂	---	0.070	45**	3.2**

* Carbon black Type AB, 42 m μ average diameter.

** Calculated from the aliphatic hydrocarbon data.

Table III
 BEHAVIOR OF CANDIDATE PARTICULATE GELLANTS IN
 n-HEPTANE AND LIQUID NITROGEN

Material	Nominal Particle Size μ	Density g/cm ³	Observation		Yield Stress of LN ₂ Gel dynes/cm ²
			n-Heptane (w/o)	Liquid N ₂ (w/o)	
Alumina (pyrogenic)	30	3.6	Thickened at 12.5	Settled out, wetted	---
Alumina (lamellar)	5000 x 20	3.5-3.9	Gel at 8-10	Settled out, wetted	---
Carbon Black (HCC)	7	1.75	Thin gel at 15	Settled out, wetted	---
Conductive Furnace (Carbon) Black	29	1.75	--	Gelled at 8.5	370
Acetylene Black	42	1.95	Gel at 9	Gelled at 5.5	300
Silica, H-5	7	2.2	Gel at 6	Gelled at 4.6	380
Titania, P-25	33	4.26	Thickened at 12.5	Thick at 10-15	---

3. Solid Fuels as Gellants

Three fuels which have shown promise as gellants in other systems (4) were tried as gellants in liquid nitrogen. They are amorphous boron, fine-ground boron carbide, and flake aluminum. Light metal hydrides and an ultrafine spherical aluminum were also investigated.

a. Boron

Two grades of amorphous boron were tried. The first is a standard grade, of 90-92 percent purity, and average particle size 1 μ , and the second a higher purity (94-97 percent) grade of average particle size 1.2 μ . Because of their relatively large particle size, they were not expected to form gels at concentrations below 35 w/o, but success at this level would justify attempts to prepare ultrafine powder.

Using the special mixer designed for the cryostat, but in an ordinary Dewar flask, portions of the boron were added to liquid nitrogen until thickening was apparent. Then smaller portions were added, with pauses established for observation of gel-like behavior.

The standard amorphous boron gave a gel with apparent yield stress, estimated to be 300 dynes/cm², and thixotropy at 33 w/o. The higher purity boron did not show such behavior even up to 48 w/o, but settled out when the mixer was stopped.

Boron appeared of possible interest as a candidate high-energy fuel-gellant for hydrogen. A possible source of ultrafine boron powder is being investigated, for future trials (4).

(1) Boron Grinding

Attempts were made to reduce the size of the amorphous boron (90-92 percent purity) which gelled liquid nitrogen at 33 w/o. This boron had a particle size of about 1 μ , with aggregates extending to 20-30 μ . Since it was not protected from air during shipment, the surface is probably oxidized. It was further ground in a pebble mill under nitrogen, at near liquid-nitrogen temperature. Microscopic examination revealed that the aggregates were well broken up.

When tried as a gellant, the milled boron failed to gel liquid nitrogen at 35 w/o. Some particle size reduction had been effected, and this normally should have decreased the amount needed for gelling. However, the fresh surfaces exposed by the grinding, perhaps directly or through reaction, have offset the gain achieved by particle size reduction. This underscores the importance of the surface chemistry of the particles for optimum gelling efficiency.

b. Boron Carbide

Abrasive grade boron carbide is available in a 4-8 μ particle size. Under the same conditions as with boron, above, this material thickened liquid nitrogen at 41.4 w/o, showing evidence of yield stress and shear-thinning.

Boron carbide will also be considered a candidate energetic fuel-gellant for liquid hydrogen. Although finer particles are not currently available, preparations might be more readily accomplished than for elemental boron since boron carbide is more inert and more friable than boron. Presently available boron carbide is obviously too large for use as a gellant for liquid hydrogen.

c. Aluminum

Aluminum flake of the finest particle size available (approximately 20 $\mu \times 0.04 \mu$) was tried as a gellant in liquid nitrogen. It formed a gel at 31.8 w/o, with a yield stress of 390 dynes/cm², and shear-thinning properties.

The flake aluminum was known to contain a trace amount of stearic acid (a lubricant in the forming process). When this was removed by extraction with hexane, the aluminum flake would no longer gel liquid nitrogen.

An ultrafine spheroidal aluminum (average diameter 30 m μ), passivated by oxidation to the point where it was non-pyrophoric, was tried without success as a gellant in liquid nitrogen. Similar sized material which had not been passivated was tried in liquid nitrogen with the same result. No thickening occurred up to 50 w/o.

d. Lithium Borohydride (LiBH₄)

Lithium borohydride offers three possible advantages as a particulate gellant for liquid hydrogen: It will contribute energy, as a fuel; it contains a high percentage of hydrogen, and hence may have the requisite surface affinity for liquid hydrogen; and it has a very low density (0.66 g/cm³) which should minimize the w/o needed for gelling and/or permit a slightly larger particle size than denser gellants. Calculations of its influence on I_{sp} are shown in Section V. Preliminary efforts to prepare it in particle size fine enough for gelling are described under Section B. According to Figure 2, particles averaging 6.5 m μ in size would be necessary to gel LH₂ at 5 w/o.

e. Lithium Aluminum Hydride (LiAlH₄)

Lithium aluminum hydride has the same three potential advantages as lithium borohydride as a gellant for liquid hydrogen, although to a lesser extent. (Its density is 0.92 g/cm³ and its heat of combustion, per unit mass, is slightly lower than that of lithium borohydride). It was more readily available at the beginning of the program, and it was

therefore used for working out precipitation procedures, as described under Section B. When it became apparent that LiBH_4 was more promising, work on LiAlH_4 was discontinued.

f. Other Solid Fuels

In a concurrent program in our laboratories (4), various high-energy solid fuels are being investigated as candidate gellants for conventional liquid propellants, ranging from the non-polar hydrocarbons to highly polar hydrazine. Some of these, which look promising in the hydrocarbons, should also be considered candidate gellants for LH_2 .

Two of them, boron and boron carbide, have been screened in liquid nitrogen and are discussed above (a. and b.). Two others which show potential for hydrogen are Olane 58, and dilithium acetylide (Li_2C_2). Pertinent gelling data are as follows:

	<u>Particle Size</u>	<u>Gel</u>
<u>Olane 58</u>		
S-186	-325 mesh	No Gel
S-168	-400 mesh	50 w/o (n-heptane)
S-217	3-5 μ	22 w/o (n-heptane)
<u>Dilithium Acetylide</u>		
Ethylenediamine complex		35 w/o (n-heptane)
Non-complex, generated <u>in situ</u>		10 w/o (hexane)

The non-complexed dilithium acetylide was formed by passing a stream of acetylene into a solution of butyllithium in hexane. Isolation of this precipitate in the dry state presented certain hazards, so the dry, stable ethylenediamine complex was used for the first gelling trial in liquid nitrogen. A gel was formed at 28.5 w/o, with an estimated yield stress of 300-400 dynes/cm² and good shear-thinning properties.

4. In Situ Gelation, Using Liquid and Gaseous Fuels

The common processes for making particles in the $<0.1 \mu$ size range nearly all consist of generating the material in the vapor phase under conditions such that it will condense immediately as a solid. Carbon blacks, and pyrogenic silica and alumina are examples of gellants, used in this investigation, which are made in this way. Additionally, vaporization and condensation has been used for similar preparation of ultrafine particles of metals such as aluminum, nickel, and iron.

It appeared logical, therefore, to apply this technique to certain somewhat energetic gaseous and liquid fuels, since they might be caused to condense in the desired ultrafine particle size upon sudden exposure to the low temperature in the liquid hydrogen cryostat.

a. Pentane

As a first experiment in in situ formation of gellant particles, n-pentane was introduced into liquid nitrogen by bubbling in gaseous nitrogen saturated with pentane vapor. Fine crystals of pentane formed in the liquid nitrogen, and showed a thickening effect, but freezing out in the feed tube occurred. It appears that with controlled nucleation conditions, gelation by this technique might be possible.

b. Propane

Since propane freezes at -190°C , which is above the boiling point of nitrogen (-196°C), it was used in an exploratory experiment to simulate the methane/liquid hydrogen system. Propane gas, mixed with dry nitrogen, was bubbled into liquid nitrogen in an attempt to form ultrafine crystals of solid propane. The propane did not solidify, but formed a liquid layer which floated on the nitrogen. Possibly an insulating gas layer existed at the interface which prevented adequate cooling of the propane, or it may have been supercooled.

To provide nucleation sites for the crystallization of the propane, small amounts of pyrogenic silica and of acetylene black were suspended in liquid nitrogen prior to the bubbling in of propane. Coagulation resulted in the experiment with silica, but in the experiment with acetylene black, a gel formed which showed shear-thinning properties and had a yield stress estimated to be 300-400 dynes/cm².

c. Methane

Methane contains the highest percentage of hydrogen of any hydrocarbon, which might give it the requisite affinity for liquid hydrogen. It is also very low in density (about 0.4 g/cm³) and has a reasonably high fuel value. Hydrocarbons are representative of non-polar, essentially non-associated gellants.

Methane is a solid at the boiling point of liquid nitrogen. Accordingly, attempts to crystallize methane as fine particles were made by adding it, as gas and as liquid, to liquid nitrogen. However, on mixing, only an apparent increase in volume of the LN₂ was observed, indicating solubility, and no insoluble material was observed.

d. Ammonia

Ammonia, like methane, has a large hydrogen content, and might therefore have enough affinity for liquid hydrogen to be a satisfactory

particulate gellant. Unlike methane, ammonia is a relatively polar liquid, nearly as polar as water, and is highly associated. Thus it represents an entirely different type of solid particulate surface.

Bubbling gaseous anhydrous ammonia into liquid nitrogen produced a cloudy appearance, and some crystals formed on the sides of the Dewar flask. However, when liquid ammonia was added to liquid nitrogen with high-shear mixing, an apparent solution resulted. A trace of carbon black failed to nucleate crystallization.

In further attempts, liquid nitrogen was put in the enclosed inner vessel of the liquid hydrogen cryostat, to permit control of the atmosphere above it. A bleed-stream of helium with 6 v/o ammonia, pre-cooled to -50°C by an acetone-dry-ice trap, was fed into the space above the liquid nitrogen. The ammonia condensed as a cloud, the particles of which fell into the liquid nitrogen, forming a slurry. The particles appeared to be less than $0.1\ \mu$ in size, as evidenced by the reddish color of transmitted light, due to diffraction around the small particles. The addition of helium and ammonia was continued, with mechanical stirring of the nitrogen, until a slurry containing about 50 w/o of ammonia particles had been formed. When mixing was stopped, the ammonia particles settled out.

Ammonia was thus successfully condensed as fine solid particles from a pre-cooled bleed-stream of helium and ammonia. The particles formed may not have been fine enough to form a gel (and possibly there was crystal growth due to solubility) but the technique, with refinements to achieve smaller particle size, should be applicable to liquid hydrogen.

5. Surface Treatment of Gelling Agents

Optimum gellant performance in liquid hydrogen may require a surface-active third component, to form an oriented film on the gellant particles. It was not known whether the bonding and associative effects of surfactants would function at cryogenic temperatures. Furthermore, such surfactants are usually added directly to a mixture of gellant and liquid, their affinity for the liquid enabling them to migrate to the solid-liquid interface. If added to liquid hydrogen, such surfactants would freeze. It is therefore necessary to precoat the gellant particles and thus pre-orient the surfactant.

A brief investigation was carried out to determine if surfactants function at liquid nitrogen temperatures and to serve as a model for gellant surfactant addition. Portions of pyrogenic silica were treated with 3 w/o of selected surfactants in very dilute ether solutions. The surfactants had previously been shown to affect gelling action in low-polarity liquids (1).

These portions were dried at 50°C to remove the ether, and tested for gelling ability in liquid nitrogen, using untreated silica as a control.

Untreated silica formed a gel at 4.6 w/o. Silica treated with Triton X-100 formed a poor gel at 16 w/o. Despite the normal appearance of the other four treated silicas, they failed to disperse in the liquid nitrogen.

The observed effect of Triton X-100 causing the need for more gellant indicates that surfactant effects can occur under cryogenic conditions. Further experimentation with these and with other surfactants will be necessary to establish guide lines for their use in LN_2 .

B. Preparation of Fine Particles of Gellants

1. Lithium Aluminum Hydride (LiAlH_4)

Lithium aluminum hydride is normally available in lump form. It is soluble to some extent in ethers, and insoluble in hydrocarbons, suggesting a simple solvent/non-solvent system for precipitation of fine particles.

a. Ethyl Ether/Hexane

Experiments were run in which the LiAlH_4 was dissolved in ethyl ether, and precipitated by the addition of hexane. Evidence of reaction with the solvents, the formation of a large amount of dark, insoluble material, and an oily precipitate suggested that another system might be better.

b. Tetrahydrofuran/Heptane

Tetrahydrofuran (THF), in which the solubility of LiAlH_4 appeared higher than in ethyl ether, and n-heptane were pre-treated with LiAlH_4 to remove all reacting impurities. A 10 w/o solution of LiAlH_4 in THF was then prepared and filtered through fritted glass. When 7 volumes of heptane were added with rapid agitation, an oil separated, which on standing 48 hours solidified into a white, crystalline mass.

The supernatant liquid was discarded and the crystalline material was redissolved in treated THF, forming a clear solution. Heptane (5:1) was chilled over liquid nitrogen, and the THF solution added with high-shear mixing. Despite these conditions, the precipitate was oily in nature and quickly agglomerated in the bottom of the vessel.

The behavior of the precipitate indicated that it might be an ether-type solvate. In order to better separate solvent complexes, a lower boiling solvent and boiling non-solvent were used. Lithium aluminum hydride was precipitated by adding its ethyl ether solution dropwise

Table IV
EFFECTS OF SURFACTANT COATINGS ON GELLING ABILITY
OF PYROGENIC SILICA IN LIQUID NITROGEN

	Action on Gels	
	In Room Temperature Liquids	In LN ₂
Pelargonic acid	Enhanced	Settled
Triton X-100 (Octylphenyl ether of polyethylene glycol)	None	More SiO ₂ required
AMP (2-amino, 2 methylpropanol)	Destroyed gel	Settled
Duomeen T (Tallow diamine)	Enhanced	Settled
Alamine 4 (Primary lauryl amine)	Slightly enhanced	Settled

to boiling hexane, with the ether distilling instantly. The resulting fine-particle precipitate, after collection and drying, showed electrostatic properties and a high tendency to agglomerate. The bulk density was about 0.43 g/cm^3 .

In the Whitby centrifuge sedimentation analysis for particle size, it was not possible to overcome the agglomerative tendency, and hence no size distribution data were readily obtained. Microscopic examination revealed many agglomerates of $100\text{--}200 \mu$ size, but the individual particles appeared to be no larger than 12μ , ranging down to 1μ and smaller.

This lithium aluminum hydride was given a preliminary trial in liquid nitrogen. Although gelling at a low concentration was not expected because of the rather large quantity of coarse particles, at 45 w/o a thickened mixture with some evidence of gel structure and shear thinning resulted. Later, greater success with LiBH_4 , a more desirable gellant material, led to suspension of effort with LiAlH_4 .

2. Lithium Borohydride (LiBH_4)

a. Particle Fracture Techniques

The technique of preparing LiBH_4 by prolonged grinding with mortar and pestle under an inert atmosphere (N_2) in a dry box was used as an expedient to secure powdered material for compatibility testing with LH_2 . Experience indicates that when long grinding times are used, a modest fraction of submicron particles is obtained. Microscopic examination revealed little or no hazy background, normally indicative of submicron particles, but the visible particles were in the 10μ size range. This preparation was used in subsequent gelling of LH_2 .

Microscopy indicated that the LiBH_4 recovered from the LH_2 experiment was somewhat finer than that added. There was the appearance of a faint haze and the number of below 10μ particles apparently increased. It would seem that the crystals may become brittle enough at cryogenic temperatures to fracture readily.

b. Solvent/Non-Solvent Precipitation

(1) Tetrahydrofuran/Heptane

Attempts were made to precipitate LiBH_4 as fine particles from a tetrahydrofuran (THF) - heptane system. A 10 w/o solution of LiBH_4 in THF was prepared and filtered. When heptane was added to this in any ratio from 1:1 upward, it failed to mix. In spite of prolonged high-shear mixing in a "laboratory mixer", the THF solution separated as a distinct layer, although THF and heptane are normally miscible.

(2) Ethyl Ether/Hexane

The ethyl ether/hexane technique worked out for the precipitation of fine-particle lithium aluminum hydride (LiAlH_4) was extended to LiBH_4 .

The ethyl ether (solvent) and hexane (non-solvent) were first treated with lump LiAlH_4 to eliminate reactive impurities, and then distilled. LiBH_4 was dissolved in ether, the solution was filtered, and it was then added slowly to boiling hexane at a rate whereby most of the ether distilled off as fast as it was added. (In spite of this, the LiBH_4 which precipitated out appeared to be an etherate, as evidenced later). After all of the ether solution was added, distillation of hexane was continued until the boiling point indicated that no more ether was being removed. The precipitated LiBH_4 was collected by filtration, and dried at room temperature under vacuum, using a LN_2 trap to condense the vapors. While the drying was taking place, the material gave the appearance of a fluidized bed of fine powder, and the liquid collected in the trap was mostly ethyl ether.

The LiBH_4 prepared in this manner appears to be much finer than that prepared by grinding. Microscopic examination showed the material to be mostly needle-shaped unagglomerated particles in the 2-5 μ size range, with a considerable haze probably due to sub-micron particles. Standard sedimentation methods of size estimation (e.g., The Whitby Technique) are not directly applicable here since they require the use of a liquid sedimentation medium of substantially lower density than the LiBH_4 ($\rho = 0.66 \text{ g/cm}^3$). In a small-scale check with heptane, the precipitated LiBH_4 formed a gel at 19 w/o.

Additional material was prepared by this method for the liquid hydrogen gelling experiments.

(3) Ethyl Ether/Toluene

As the ethyl ether/hexane method had apparently precipitated an etherate rather than uncomplexed LiBH_4 , a higher boiling non-solvent, toluene (b.p. 110°C) was substituted for hexane (b.p. 69°C) to facilitate instant removal of the ether. This appeared to be successful.

Microscopic examination showed the particles of dried LiBH_4 to be nearly spherical, with apparent diameters in the 1-12 μ range, and some evidence of a haze of smaller particles. In a trial with n-heptane, this material formed a gel at 28 w/o, as compared with 19 w/o for the ether-hexane precipitated material. It appears that the break-up of the etherate during vacuum-drying of the hexane-precipitated LiBH_4 favored the formation of very fine particles.

IV. GELATION OF LIQUID HYDROGEN

A. Initial Gelling Experiments With Various Gellants

1. Carbon Black

For the first gelling trials, carbon black (Type AB) was selected as the candidate gellant. It was prepared and placed in the cryostat as described in the Appendix. When it was added to the liquid hydrogen, there was no rapid boiling or pressure surge, showing that it had been adequately pre-cooled, and there was no large heat release due to wetting by H_2 or H_2 adsorption. It was subsequently found that not all of the carbon black was released from the bag, and the concentrations have been corrected for this value. Table V shows these concentrations.

The mixer was operated at blade-tip peripheral speed of 230 ft/min (computed from the rotational speed as measured with a Strobotac). Although it had been planned to run it at higher speeds, there was a misalignment problem and excessive shaft whip. Experience in gelling other fluids indicates that carbon black probably does not require extreme shear to develop adequate gelling action.

During mixing, the carbon black was suspended in the liquid hydrogen, but each time the mixer was stopped, the carbon black settled rapidly. The volume to which it settled was several times the volume occupied by this amount of dry carbon black, and increased slightly after each early mixing. After repeated mixings, it settled each time to the same level, indicating no further physical change in dispersion or wetting. The composition of the lower stratum was 1.4 v/o carbon black (28 w/o). This expanded sedimentation volume in other work has been taken as evidence of a threshold of interparticulate forces interaction, and of incipient gelling.

The liquid hydrogen was forced to evaporate to various levels (thus increasing the concentration of gellant) but there was still visible settling of the carbon black.

In the experiments with n-heptane and liquid methane reported above (Section III B. 2), slightly more than 3 v/o of carbon black Type AB was required for gelling. In LH_2 the carbon black showed evidence of a threshold of interparticle forces at 1.4 v/o. It is reasonable to expect that a gelling concentration might be found somewhere between this concentration and 3+ v/o.

* General experimental procedures and cryostat are described in the Appendix.

Table V
OBSERVATIONS DURING GELLING EXPERIMENT
WITH LIQUID HYDROGEN AND CARBON BLACK

<u>Condition</u>	<u>Total Volume ml</u>	<u>Carbon Black*</u>		<u>Remarks</u>
		<u>w/o</u>	<u>v/o</u>	
After initial dispersal	550	9.5	0.4	Settled rapidly
After deliberate evaporation	280	17	0.8	Settled
Composition of sedimented stratum	150	28	1.5	---

* 4.0 g Type AB, $\rho = 1.95 \text{ g/cm}^3$.

2. Pyrogenic Silica

This candidate gelling agent was selected because it is a particulate material the behavior of which has been well defined in many liquids at room temperature and in this present work, in LN_2 . It has perhaps the smallest particle size, and, nearly the lowest density, of the commercial gellants.

The pyrogenic silica was maintained at 100°C under vacuum ($5 \mu \text{ Hg}$ pressure) for three hours to remove adsorbed gases. The vacuum was released with helium gas. The silica was positioned in the cryostat as described in the Appendix.

When the gellant bag was opened and silica mixed with LH_2 , there was no evidence of heat release (i.e., no flashing or bubbling occurred). Only 9.2 gm of the silica left the container, so that concentrations are adjusted for this value. The mixer was operated at peripheral speeds up to 630 ft/min for 20 minutes. Experience in gelling other fluids has indicated that this level of stirring is adequate for gelling action.

The material in the inner vessel was semi-translucent from initial suspension stages through gel formation.

Table VI gives the successive important concentrations.

When the volume had diminished by evaporation to 220 ml, a gel formed (estimated yield stress 400 dynes/cm^2) which showed no syneresis nor measurable evaporation on standing 30 minutes without stirring. Hand manipulation of the mixer indicated the gel was thixotropic. One could create an irregular surface and induce flow by more rapid shearing. The gel had the appearance of a typical adhesive gel.

This gel of LH_2 , while not suitable for propellant use because of its high inert (SiO_2) concentration (37.7 w/o or 1.9 v/o), is interesting as a possible cold flow simulant (average density = 0.11 g/ml vs 0.07 g/ml for neat LH_2). It also demonstrates the need for lower density, small-particle-sized gellants for practical use.

The gel appeared to be reasonably cohesive during final evaporation to dryness, in that it shrank and pulled away from the vessel sides. There was no evidence of fluffy silica on the surface until nearly dry. The silica appeared to be unchanged after complete evaporation.

3. Lithium Aluminum Hydride

This material was selected for investigation since its density ($\rho = 0.92$) is considerably more favorable than that of silica, it has fuel value, and was usable as a reasonable prototype of other light metal hydrides insofar as fine-particle preparative methods were concerned.

Table VI
OBSERVATIONS DURING GELLING EXPERIMENT
WITH LIQUID HYDROGEN AND SILICA

Condition	Total Volume ml	Silica		Sediment Volume ml	Comments
		w/o	v/o		
After initial dispersal	615	17.7	0.7		
Immediately prior to gel formation	260	34	1.6	240	
Formation of gel	220	37.7	1.9		Gelled
Thirty minutes after gel formation	220	37.7	1.9		No sign of syneresis

Fine particle LiAlH_4 , prepared by the solvent/non-solvent technique (III. B. 1., above) had gelled LN_2 and also heptane, requiring about 45 w/o gellant. Its particle size was excessive, ranging from 12μ to less than 1μ . For this trial it was outgassed under vacuum (5μ Hg pressure) at room temperature, and the pressure was released with helium. The gelling experiment was carried out in similar fashion to the silica trial, above. When the LiAlH_4 was added to the LH_2 , there was no sign of reaction or other heat release. The particles took an average of two seconds to fall through eight inches of liquid. After stirring and evaporation, the data of Table VII were obtained. The increase in sediment volume suggests that some high-shear grinding of the gellant was accomplished. A gel was observed at a volume of 75 ml. The yield stress was estimated to be between 200 and 300 dynes/cm² and, based on the behavior of the disturbed surface, the material was thixotropic. No syneresis was noted after 20 minutes of standing without mixing.

Beamed light observation of the gel indicated that it was translucent.

The LiAlH_4 content of the gel was 86 w/o and 32 v/o. The high w/o and v/o values were attributed to larger-than-desired particle size of the LiAlH_4 .

The gel shrank during final evaporation, but unlike the silica, did not pull away from the vessel sides. There was some powdery surface appearance during the later stages of evaporation.

4. Lithium Borohydride

This gellant ($\rho = 0.66 \text{ g/cm}^3$) is the most favorable of the present candidates on a density basis. Although initially only a preparation thoroughly ground under an inert atmosphere was available, it was used to obtain compatibility information. The LiBH_4 was outgassed under vacuum (5μ Hg pressure) at room temperature, and the vacuum was released with hydrogen. When the LiBH_4 was added, there was no noticeable heat release. The particles took an average of two seconds to settle through eight inches of LH_2 . The sediment volume was 125 ml after stirring at mixer peripheral speeds of 450 fpm. Reduction of LH_2 volume coupled with continued agitation led to a sudden change in sediment volume to 190 ml, indicating particle size reduction through high-shear grinding. When the over-all volume was reduced to 200 ml, an apparent gel formed with a yield stress of 200-300 dynes/cm². The results are delineated in Table VIII. After standing for over 30 minutes without agitation, there was still no sign of syneresis.

Movement of the observation light at various angles indicated the gel was semi-translucent, but not quite so translucent as that formed with LiAlH_4 . Manipulation of the mixer indicated this gel was thixotropic. It appeared to adhere somewhat to the vessel walls, and on further evaporation behaved in similar fashion to the LiAlH_4 gel.

Table VII

OBSERVATIONS DURING GELLING EXPERIMENT WITH
LIQUID HYDROGEN AND LITHIUM ALUMINUM HYDRIDE

Condition	Total Volume ml	LiAlH_4		Sediment Volume ml	Comments
		w/o	v/o		
After initial dispersal	740	30.5	3.2		
Immediately prior to gel formation	80	85	30	70	
Formation of gel	75	86	32	--	Gelled
Twenty minutes after gel formation	75	86	32	--	No syneresis

Table VIII
OBSERVATIONS DURING GELLING EXPERIMENT WITH
LIQUID HYDROGEN AND LITHIUM BOROHYDRIDE

Condition	Total Volume ml	LiBH ₄		Sediment Volume ml	Comments
		w/o	v/o		
After initial dispersal	850	29	4		
After deliberate evaporation	480	43	7	125	
Immediately prior to gel formation	260	60	13	190	
Formation of gel	200	67	17	-	Gelled
Twenty minutes after gel formation	200	67	17	-	No sign of syneresis

The LiBH_4 composition of the gel was 67 w/o and 17 v/o. These results were particularly encouraging considering the large particle size preparation used. Further reduction in particle size should produce a more desirable gel composition.

After evaporation of the hydrogen, the residual LiBH_4 was checked for gelling ability in heptane. It formed a smooth gel at somewhat more than 20 v/o.

5. Aluminum Flake

Flake aluminum with a average flake thickness of 0.04μ was held under vacuum (at 5μ Hg pressure) at room temperature for three hours. The vacuum was released with ultra-pure hydrogen (less than 3 ppm impurities). The cryostat was assembled with 70 grams of treated aluminum positioned in the usual gellant bag.

Release of the aluminum into the LH_2 produced a fine dispersion which had a tendency to settle within 4 seconds after the mixer was stopped. During agitation with mixer peripheral speeds of 300-450 fpm, some gel-like material clung to the glass vessel wall. When enough weight accumulated, the lump of material slid down the glass wall, leaving it clean, indicating that the gel was relatively non-adhesive. Visual observation was very difficult due to the tendency of the reflective powdered aluminum to coat the wall of the vessel, both above and below the liquid level.

An opaque gel which was thixotropic (as shown by its behavior on the mixer shaft and glass vessel walls) was formed at about the 350 ml level. The aluminum content at this stage was 73 w/o and 7.5 v/o.

6. Methane (In Situ Gelation)

Methane (CH_4) contains the highest percentage (25%) of hydrogen, has the lowest density (solid = 0.4 g/cm^3), and the highest possible energy contribution of the candidate gellants under consideration.

A preliminary attempt to condense fine particles of methane over liquid hydrogen was carried out as follows: A bleed stream of helium containing 3.4 v/o methane, precooled by a liquid nitrogen/Freon 113 slush trap, was passed into the atmosphere above liquid hydrogen in the cryostat. A cloud of methane particles formed, and the particles fell into the liquid hydrogen, some staying suspended and some settling to the bottom. The methane content of the bleed stream was gradually increased, over a 20-minute period, to 75 v/o, without any plugging of the entry port from premature condensing of methane.

The bleed stream flow rate was such that the amount of methane condensed during this trial was calculated to be only a fraction of that which would be necessary for gelling. However, the feasibility of condensing methane by this method was established, and the methane crystals

appeared to be insoluble in liquid hydrogen. As many of the particles were large enough to be visible, modifications of the apparatus and/or technique will be needed to achieve methane particles suitably small for efficient gelling.

B. Gelation of LH₂ With Selected Gellants

Of the six gellants examined in the preliminary trials above, all either formed gels or showed promise of forming gels under slightly altered conditions. Pyrogenic silica (7 μ particles) was effective, at 37.7 w/o or 1.9 v/o, making it a suitable gellant for reference comparisons and for gel property studies, even though such a mass loading of inert gellant would not be tolerable for propulsion. Such a gel is also usable as a cold flow simulant since its density is only 1.6 times that of liquid hydrogen, and its volumetric loading (i.e., volume occupied by the particles and hence the parameter of interest in flow interference investigation) is about that expected for more energetic gellants. Of the candidate energy-contributing gellants, lithium borohydride appeared most promising, gelling at 67 w/o or 17 v/o. Flake aluminum, although it gave difficulty in observation, appeared to gel at 73 w/o or 7.5 v/o. These three were then selected for the remaining experimental work in this phase of the program.

1. Lithium Borohydride (LiBH₄)

Fine particle LiBH₄ for these gelling experiments was prepared by the ethyl ether/hexane precipitation technique previously described (Section III, B, 2 (b), (2)). It was outgassed under vacuum pressure (5 μ Hg pressure) at room temperature for 4 hours and back-filled with ultra-pure hydrogen, encased in a plastic bag and placed in the cryostat as described in the Appendix.

In the first experiment, gelation occurred at 72 w/o. The estimated yield stress was 300 dynes/cm² and the average evaporation rate 3.4 ml/min. As the gel evaporated to dryness, an inert atmosphere was maintained and the dry LiBH₄ powder recovered. Microscopic examination showed it to be essentially unchanged, and a small sample gelled n-heptane at 22 w/o, as before.

The same lot of LiBH₄ was re-used for a second gelling experiment, in which rheological measurements (see D, below for details of method) showed a yield stress of 880 dynes/cm² and a marked shear-thinning effect. The gellant concentration was 74 w/o.

In a third gelling experiment, again using the same (recovered) LiBH₄, a gel with a yield stress of 1100 dynes/cm² was obtained at 79 w/o.

The slight decrease in gelling ability each time the LiBH_4 was recovered and re-used can probably be attributed to slight deterioration during handling of the dry powder, rather than to exposure to liquid hydrogen. This indicates good stability of LiBH_4 as a gellant.

2. Pyrogenic Silica

This material consists of amorphous spheres of silicon dioxide about 7 μ in diameter, and has a surface area of approximately 300 m^2/g . The surface tends to chemisorb water, forming hydroxyl (or silanol) groups. Previous work (1) has shown that maximum gelling efficiency for non-polar liquids occurs when the silica is thermally dehydrated to the point that less than 30 percent of the surface is hydroxylated.

For the first experiment, the silica used was dried 3 hours at 250°C, under vacuum (5 μ Hg pressure), and the vacuum released with helium, as described in the Appendix.

After adding liquid hydrogen to the inner vessel, the gellant bag was opened by rotating the mixer shaft, and the mixer operated until the silica was well dispersed. Initially each time the mixer was stopped the silica settled, leaving visibly clear liquid hydrogen above. After some evaporation of the hydrogen a gel formed with an estimated yield stress greater than 500 dynes/cm², at a concentration of 36 w/o (1.8 v/o) silica.

It was believed that the helium and hydrogen purges of the cryostat, prior to liquid hydrogen loading, might also serve to purge the gellant powder. Accordingly, for the next trial the silica was simply dried (overnight at 150°C) and kept dry prior to use. At 35.3 w/o (1.8 v/o) it formed a gel with a yield stress of 1210 dynes/cm². This showed that prior outgassing of silica is probably not necessary.

Similar gels were prepared, with comparable silica concentrations and yield stresses, for the further study of evaporation rates, rheology, and effects of vibration and acceleration. These are reported in subsections C, D and E, below.

3. Aluminum Flake

One confirmatory gelling trial was made with flake aluminum (size 20 x 0.04 μ) (Alcoa No. 422). The aluminum powder was outgassed at 5 μ Hg pressure, at room temperature, and back-filled with helium, then positioned in the cryostat as described in the Appendix. A gel formed in liquid hydrogen at 79 w/o (8.1 v/o) aluminum. The opacity of the gel and its tendency to coat the viewing ports of the cryostat made further visual observations (i.e., evaporation rate) difficult.

C. Evaporation Rate of LH₂ Gels

Evaporation rate data were obtained for each of several LH₂ gels, under the conditions where there was no LH₂ in the Dewar surrounding the inner vessel. In all cases an excess of LH₂ was charged initially, and allowed to evaporate, with intermittent mechanical stirring (15 sec every 3 min), until the gel formed. Stirring was then discontinued, and the time for complete evaporation of the hydrogen from the gel recorded. Results are shown in Table IX.

In the case of the 72 w/o LiBH₄ gel, there was at first a shrinkage of the gel with a drop in the visible surface, representing an evaporation rate of 1.2 ml/min. After this there was no visible change, the gellant continuing to occupy the full volume while the LH₂ evaporated. In the case of the SiO₂ and Al flake gels, no shrinkage was visible at all, and the rates reported are the average from gel formation to total dryness.

A control run with non-gelled LH₂ showed a relatively uniform rate of evaporation, from 600 ml to dryness, averaging 4.7 ml/min. With one exception, the observed evaporation rates for the gels were less than half of this. (Difficulty in observing the point at which evaporation is complete is experienced with opaque gels).

It is of interest that just prior to gel formation, that is, with greatly thickened rather than gelled liquids, the evaporation rates were similarly markedly reduced. This tends to support the hypothesis that the observed reduction in evaporation rate is related to reduced convection.

D. Rheology of LH₂ Gels

Measurement of the rheological properties of gelled liquid hydrogen presented problems because of the extremely low temperatures at which none of the commercially available viscometers is suitable for operation. Although it is conceivable that certain of the standard viscometers could be modified to permit operation at 20°K, there are other limitations in commercial viscometers in studying the complex rheological properties of gel systems.

Perhaps the most important single rheological parameter in any gel for rocket use is the yield stress, which is the maximum force that can be applied to a gel without causing structure breakdown which leads to flow. It is the yield stress of a gel that inhibits flow of spilled materials, that prevents sloshing in missile tankage, that leads to reduced evaporation rates, and that permits the suspension of solid particles to form stable slurries. It is imperative that measurements of the yield stress be made by increasing the stress of the gel until flow occurs rather than by the often-used procedure of measuring apparent viscosity at gradually decreasing rates, and extrapolating to zero.

Table IX
COMPARATIVE EVAPORATION RATES
FOR GELLED AND NON-GELLED LH_2

Gellant		Evaporation Rate, ml/min	
Type	w/o	Just Before Gel	Gel
None	0	← 4.7 ave. →	
LiBH_4	72	2.7*	1.2
Al flake	79	1.0*	(a)
SiO_2	36	2.0*	2.2
SiO_2	39	-	3.1

(a) = not observable.

* Thickened liquid but no yield stress.

Gels of the type which are suitable for use as liquid propellants shear-thin rapidly with increasing rate of shear. Thus the gel will exhibit appreciable apparent viscosity when the applied shear stress just exceeds the yield stress. However, as the shear rate increases to that experienced by the gels in tankage flow and in rocket injectors (10^5 to 10^6 sec^{-1}), the apparent viscosity decreases to a value only slightly greater than that of the unmodified liquid.

Since LH_2 must be maintained at all times under a hydrogen or helium atmosphere, the introduction of a viscometric device through the cover of the cryostat into the 2-1/2-inch diameter inner vessel, after gel preparation, presented another problem. In order to provide controlled clearance for shear-stress calculations it would be necessary to remove the mixer.

Utilizing experience in viscometer design from previous projects (5, 6), a simple device was designed and constructed which combined the mixing impeller and viscometer rotor on a single shaft, as shown in Figure 3. This shaft was driven, from above the cryostat, by either a high-speed motor for high-shear mixing, or by a commercially available viscometer drive unit, for yield stress and shear-stress/shear-rate data. The viscometer drive unit consisted of a synchronous motor, multiple speed gear box and a torque dynamometer.

The yield stress of the gel is determined by momentarily engaging the gear box to apply torque in small increments. The yield stress is computed from the maximum reading of the dynamometer before motion of the rotor is encountered. Shear stress-shear rate values are obtained by driving the rotor at a constant speed. From the known constant speed of the rotor, the shear rate can be computed. Shear stress is calculated from the reading of the torque dynamometer.

Table X lists the yield stress values obtained for the gels made in the latter part of this program, and Figure 4 shows a shear-stress/shear-rate curve for a typical LH_2 gel with pyrogenic silica. The yield stresses are generally in the range from 500 to 1200 dynes/cm², indicating reasonable resistance to flow but in the pumpable region. The curve shows pronounced shear-thinning at steady-state shear-stress/shear-rate points within experimental accuracy, the down curve of the hysteresis loop lay exactly on the upcurve. The absence of a hysteresis loop, with increasing and decreasing shear rates, indicates negligible irreversible thinning effect (persistence of reduced apparent viscosity as shear-rate is reduced). This is consistent with prior experience with liquid propellants and particulate gellants.

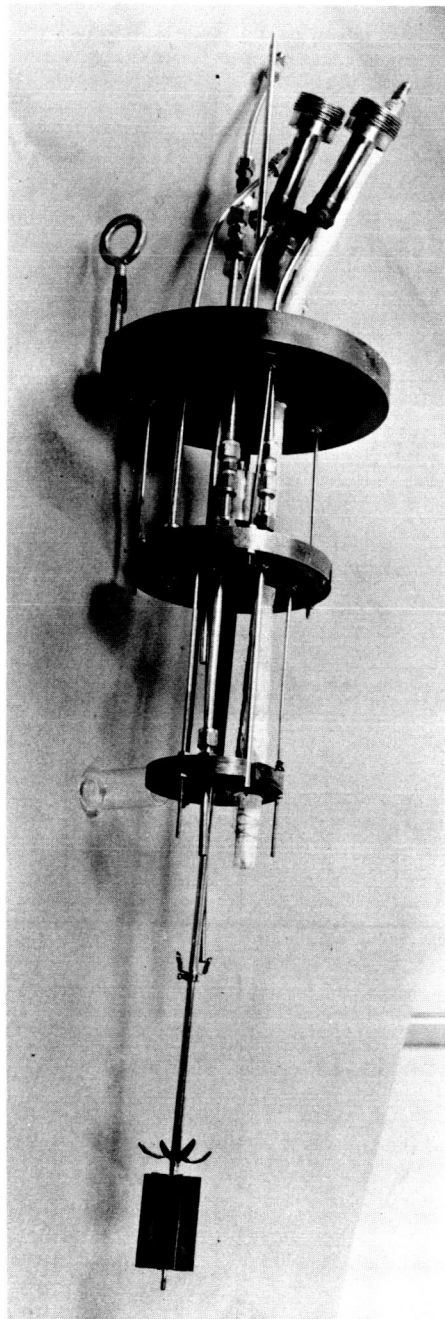


Figure 3

HIGH-SHEAR IMPELLER AND COMPATIBLE
VISCOMETER ROTOR ON SINGLE SHAFT

Table X
YIELD STRESSES OF LH_2 GELS

Type	Gellant		Yield Stress dynes/cm ²
	v/o	w/o	
LiBH_4	23	74	880
SiO_2	1.8	35.3	1210
SiO_2	1.8	35.7	550*
LiBH_4	29	79.3	1110

* Also shown on rheological curve,
Figure 4.

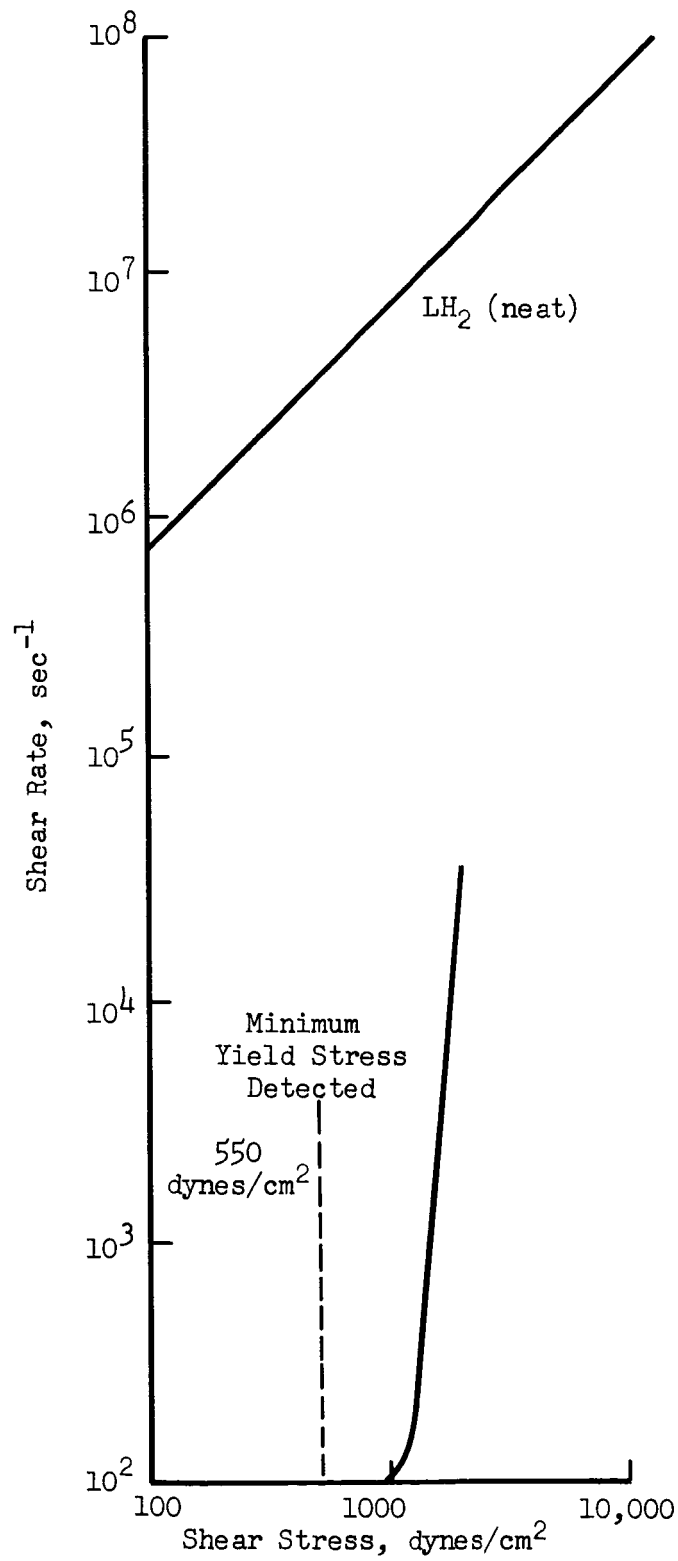


Figure 4

FLOW CURVE FOR LH_2 GELLED WITH SILICA 35.7 W/O (1.8 V/O)
(Identical curve obtained with both increasing and decreasing shear)

E. Vibration and Acceleration Resistance

A liquid hydrogen gel prepared with pyrogenic silica was subjected to low frequency vibratory acceleration by the following technique: A cup 1/2 inch in diameter by 1-inch high was suspended in the gel by means of a metal rod passing through the cover of the cryostat. The emerging end of this rod was attached to a vibrator with a frequency of 120 cps and an acceleration rate of 3 G.

The vibrator was activated for 30 minutes, while the gel was observed for any signs of change, (i.e., breakdown, syneresis, etc.). At the end of this period there was no evidence of change in the gel properties.

To test resistance to shock acceleration, the emergent end of the rod holding the cup device described above was attached to a horizontal thin steel plate. The cup was filled with gel and raised 1 inch above the surface of the bulk of the gel in the inner vessel, and a collar was attached to the rod so as to permit only 1/2 inch of downward motion. A steel ball weighing 45 gm was dropped 4 feet to impact on the plate and impart a 14 G shock to the gel in the cup. The gel motion followed that of the cup. This was repeated for a total of 30 times, with no visible effect on the gel.

V. CALCULATED EFFECT OF LiBH_4 GELLANT ON LH_2 PROPULSION PERFORMANCE

In order to estimate the effect of LiBH_4 on the propellant performance of LH_2 , machine* calculations were made of the specific impulse (shifting basis) for two levels of LiBH_4 content, and for fluorine and oxygen, separately, as the oxidizer. These results are shown in Table XI.

Two conservative boundary assumptions of the required gellant concentration were used. When LiBH_4 is prepared in particle size fine enough to gel LH_2 at 20 w/o (2.56 v/o), the degradation of theoretical impulse would be only 4.5 percent for performance with oxygen, or 2.5 percent for performance with fluorine. 10 w/o gels, if achievable, would show decrements of 4.0 percent and 1.9 percent, respectively. An earlier theoretical analysis (1) shows that gelling at 2.56 v/o is usually feasible with spherical (or nearly equiaxed) particles.

The fairly small drop of theoretical I_{sp} on increasing the gellant concentration from 10 w/o to 20 w/o may be indicative that the I_{sp} vs LiBH_4 concentration may be approaching a minimum value at 20 w/o, or indeed the minimum may lie between 10 w/o and 20 w/o. Calculations were made at only two gellant concentrations, and the exact shape of the gellant concentration vs I_{sp} curve can not be specified from the available data. Analogous calculations made by Gordon and Lee** for the tripropellant systems H_2 -B- O_2 and H_2 -Li- O_2 show the I_{sp} passing through a minimum at metal concentrations of about 8 w/o. Both curves show maxima at metal concentrations above 20 w/o. The maximum I_{sp} values are approximately 3 percent greater than the I_{sp} of the non-metallized system. Similar calculations of the H_2 -B- F_2 systems showed a continuous decrease of I_{sp} with increasing boron concentration, but the H_2 -Li F_2 system passed first through a minimum then through a maximum with increasing lithium concentration.

* IBM 7094

**L. J. Gordon and J. B. Lee, "Metals as Fuels in Multicomponent Propellants", ARS Journal 32, 600-606, 1962.

Table XI

THEORETICAL PERFORMANCE OF GELLED
(WITH LiBH_4) LIQUID HYDROGEN, WITH LOX AND LF_2

Oxidizer	LiBH_4 w/o	Ox/Fuel Ratio	I_{sp} (sec)*	Degradation %
O_2	0	3.5	391	
	10	4.15	375.5	4
	20	3.4	373.3	4.5
F_2	0	8.1	410	
	10	8.75	402.1	1.9
	20	8.0	399.9	2.5

* 1000 psia \rightarrow 14.7 psia, shifting equilibrium.

VI. SUMMARY AND RECOMMENDATIONS

This investigation of the feasibility of gelling liquid hydrogen was directed toward the ultimate goals of (a) reducing evaporation rate (b) prevention of sloshing, and (c) stabilizing slurries of additive solids. The low density (0.07 g/cm^3) and low boiling point (20.3°K) of liquid hydrogen imposed certain limiting conditions: all substances except helium are solids at this temperature and no solubility (except helium, to a slight extent) was expected.

These characteristics ruled out the swellable (i.e., partly soluble) type of gellant from consideration, and limited the search to the ultrafine particulate type. The range of candidate gellants could also include substances which are gases or liquids at ordinary temperatures. Differential density considerations indicated that the required concentration of known (inert, commercially available) particulate gellant would be so high as to cause intolerable degradation of specific impulse. Although available inert gellants were included in the feasibility determination, a search was made for low-density substances which might be prepared in ultrafine particles to serve as gellants, and which would contribute some fuel value.

For screening purposes, liquid nitrogen and liquid methane were used as cryogenic simulants for LH_2 , and hexane and heptane were used as room temperature simulants. Only those materials which gelled both types of simulant were tried as gellants for LH_2 , and all successfully gelled it, albeit at the expected relatively high concentrations.

Methane was briefly tried as a gellant in LH_2 , but only to the extent of in situ preparation of ultrafine particles. Ammonia was also briefly investigated.

Table XIII summarizes the gellants that appeared successful in LH_2 and indicates their sources. The relative gelling effectiveness is best indicated by the volume percent of gellant required, which ignores density, while the weight percent determines the practicality in a propellant system. By the volumetric criterion the two inert gellants were most effective, as was expected. Aluminum flake was the most effective of the fuels, followed by lithium borohydride. As there is little chance of preparing aluminum flake in finer size, and it will always have the disadvantage of high mass loading, it presently appears that lithium borohydride is the most promising fuel-gellant, and that further effort is warranted to prepare it in still finer particles.

Calculations of the effect on propulsion performance showed that 20 w/o (2.56 v/o, a reasonable concentration for an effective gellant) of LiBH_4 in LH_2 would reduce specific impulse only 4.5 percent for $\text{LH}_2\text{-LOX}$ and only 2.5 percent for $\text{LH}_2\text{-LF}_2$.

Table XII
SUMMARY OF GELLANTS FOR LH₂

Gellant	Particle Size, μ	Preparation	Density g/cm^3	Concentration Required	
				w/o	v/o
Silica H-5	0.007	Commercial (a)	2.2	35	1.8
Carbon black AB	0.042	Commercial (b)	1.95	45(e)	3.2(e)
Aluminum, flake	20 x 0.04	Commercial (c)	2.7	73	7.5
LiAlH ₄	1-12	Precipitated (d)	0.92	86	32
LiBH ₄	2-15	Precipitated (d)	0.67	67	17

- (a) Cab-O-Sil H-5, a commercial gellant.
 (b) Acetylene Black (highly graphitic), frequently used as a gellant.
 (c) Finest flake size, Alcoa 422.
 (d) Finest particles obtained by preparative techniques developed in this program, but not as fine as desired.
 (e) Estimated maximum values based on incipient gel at 1.5 v/o and extrapolation from hydrocarbons.

Certain other fuels also appear attractive by the criteria of low density coupled with appreciable energy contribution. Several of these appear amenable to preparation in ultrafine particles, and it is suggested that each be further investigated. They are as follows:

	Density, g/cm ³	I _{sp} with O ₂ , sec
Boron	2.33	
Lithium Hydride	0.82	263
Lithium Acetylide (LiC ₂ H)	est. > 1	
Dilithium Acetylide (Li ₂ C ₂)	1.65	
Diborane	0.44	349
Pentaborane	0.62	327
Decaborane	0.94	
Methane	0.4	309
Ammonia	0.61	

Techniques and instruments for measuring the rheological properties of LH₂ gels, within the laboratory cryostat, were developed. The thixotropic behavior of the LH₂ gels was found to be similar to that of ordinary liquids gelled at ambient temperatures; that is, there appears to be nothing different in the general behavior of a gel at 20°K. Specifically, yield stresses in the 500-1200 dynes/cm² range were achieved, along with marked shear-thinning properties. The extremely rapid recovery of gel structure after shearing apparently precluded the appearance of hysteresis loops in the rheological curves. Such absence of hysteresis appears highly desirable for LH₂ gels.

Vibrational acceleration (at 120 cps and 3 G over a 30 minute period) and shock acceleration (at 14 G for 30 shocks) produced no detectable change in a typical LH₂ gel.

Evaporation rate observations of gels in the laboratory cryostat were subject to some experimental variability, but generally showed rates only 25-50 percent of that of neat LH₂ stored under the same conditions (which included as the principal heat leak the stainless steel mixer shaft). Larger scale measurements are indicated, and are expected to show even lower rates of evaporation.

Preparation of ultrafine particles of fuel-gellants was studied by (a) various grinding methods, (b) development of solvent/non-solvent precipitation techniques, and (c) condensation of gases in the cryostat itself. These methods should be carried further in development, concurrently with a search for new sources of finer particles.

Scale-up engineering investigations are recommended in the next phase of LH₂ gel development, to establish handling requirements and characteristics, and to obtain data suitable for extrapolation to full scale storage and firing conditions.

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APPENDIXA. CRYOSTAT DESCRIPTION

For gelation studies with liquid hydrogen it was necessary to provide a vessel with observation ports, provision for moderate to high-shear mixing and rapid removal of the heat generated by it, and a means for maintaining constant volume in the working portion. A means for introducing powdered solids was also needed. No commercially available Dewar flask, of either metal or glass, had this combination of features. With the collaboration of engineers of The Marquardt Corporation*, a liquid hydrogen cryostat (Figures A-1, A-2) was assembled and used with success in the experimental work of this program. The initial design proved satisfactory to the point that only very minor modifications were necessary.

To anticipate the mixing conditions and energy release which would occur in the liquid hydrogen cryostat, several types of laboratory mixers were evaluated in a cylindrical vessel of the approximate dimensions of the cryostat proper. Standard propeller types of mixers are inapplicable in experiments of this nature, since high shear rates are frequently required for the dispersion of particulate gellants.

Suitable high-shear mixing and dispersion were effected with the use of a modification of the dual-bladed laboratory blender impeller driven by a high-speed air motor. This equipment was used successfully in the gelation experiments with liquid nitrogen, operating at low speed during the addition of the gellant, followed by a short high-speed burst to complete the dispersion and to set up the gel. At the maximum speed used, the calculated linear speed at the tips of the impeller was 830 feet per minute. Evaporation of nitrogen at this rate of mixing was only 25 percent greater than with no mixing. This mixer was used in the initial liquid hydrogen investigations. Later, this type of impeller was mounted on the same shaft as the specially designed viscometer rotor, in such a manner that neither interfered with the operation of the other.

In the design of the cryostat, consideration was given to the effect of the heat of mechanical agitation and possible liberation of heat of adsorption of hydrogen when the finely divided gelling agents were dispersed in liquid hydrogen. If the quantity of heat represented by these two factors was of considerable magnitude, dangerously rapid flash evaporation of hydrogen might occur. Since these were unknown quantities, it was decided to provide a means for adsorbing heat liberated during the experiment. This was accomplished by surrounding the test vessel with a Dewar flask containing liquid hydrogen.

* Messrs. John E. Ahern and George A. Yankura of The Marquardt Corporation supplied cryogenic engineering guidance and collaborated with Technidyne Incorporated in the design, development of procedures, and checkout for the experimental cryostat.

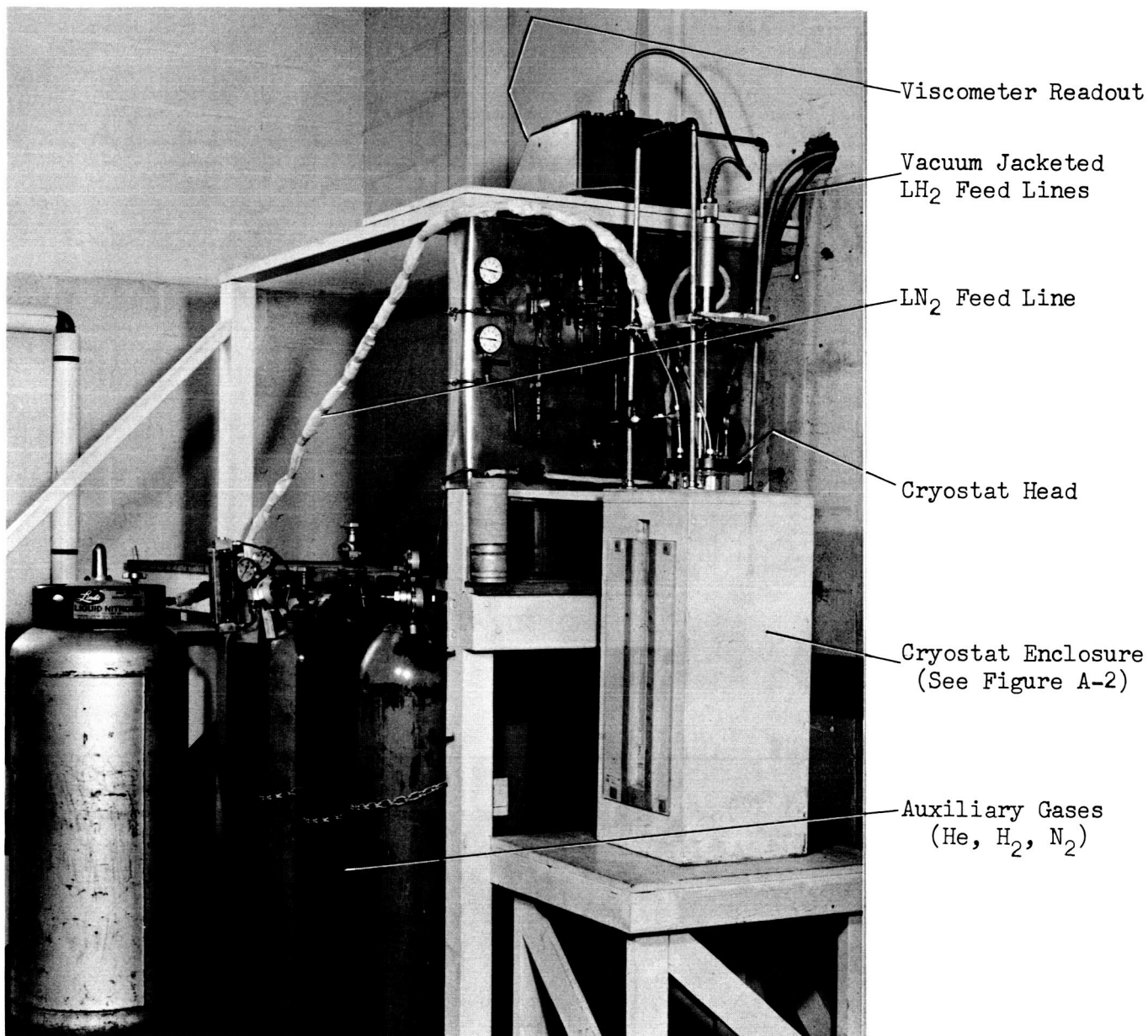


Figure A-1

LABORATORY CRYOSTAT FOR GELLING OF LIQUID HYDROGEN
(LH₂ delivery Dewar located outside of wall)

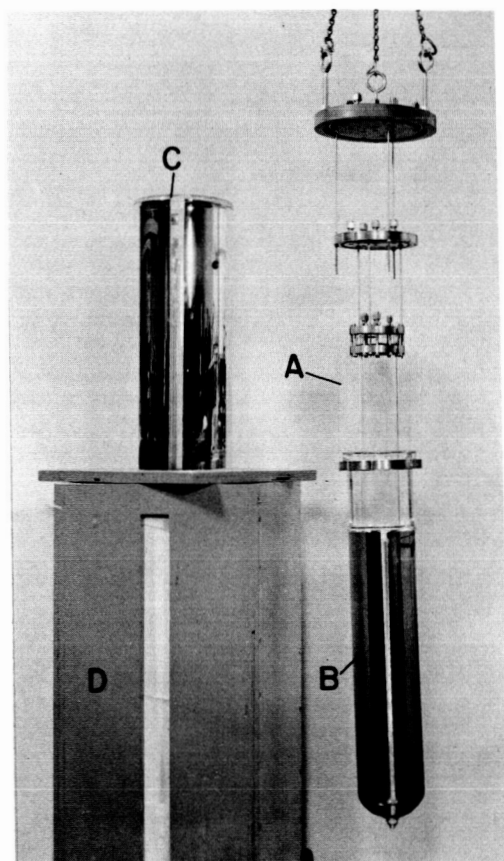


Figure A-2

LIQUID HYDROGEN CRYOSTAT FOR GELATION EXPERIMENTS

Semi-exploded view for component identification:

- A. Working Vessel. Unsilvered, cylindrical, glass, 2-1/2 inches in diameter, approximately 14 inches long. Closed by a copper flange and clamp-ring, sealed with an "O" ring of Viton A.
- B. Hydrogen Dewar Flask. To contain liquid hydrogen as heat shield. Surrounds A. Closure similar to A.
- C. Nitrogen Dewar Flask. To contain liquid nitrogen. Surrounds B. Nitrogen interposes cold shield to prevent heat loss to outside,, prevents air in-leakage if seal fails. Fitted with loose Micarta cap.
- D. Box Support. Heavy-walled, foam-plastic lined.

Each vessel is fitted with a copper-constantan thermocouple to measure temperatures. Thermocouple tubes and the 1/4-inch stainless-steel tubes for filling, evacuation, and venting enter vessels through Swagelok bulk-head fittings.

Visual observation is through unsilvered strips on flasks, lined up with window cut in support box.

The test vessel and the inner Dewar were closed by means of heavy copper flanges and clamping rings with Viton "O" rings to seal the flange to the glass. Copper was used for these parts because its high thermal conductivity would reduce thermal gradients which could cause warping and loss of the seal. The tendency to warp was further reduced by making the parts relatively thick. To further insure the maintenance of a tight closure, the glass surfaces in contact with the "O" rings were bevelled outward slightly (2°) so that the radial contraction occurring during the cooling of the copper flange would tend to increase the compression of the "O" ring. The need for these precautions arises from the fact that these flanged closures must be made up at room temperature prior to final assembly of the cryostat. If during cool-down the seals become loose, nothing remains except to abort the run, since they are inaccessible once the cryostat is assembled.

To prevent undue loss of hydrogen by evaporation from ambient heat sources, the inner Dewar flask was immersed in a larger Dewar which could be filled with liquid nitrogen. This not only served as a heat shield, but also could be used to precool the apparatus before admitting hydrogen. In addition, the slight positive pressure of nitrogen, created by the loose-fitting cover on the outer Dewar, prevents back-diffusion of air into liquid hydrogen regions.

As can be seen in the photograph of the assembly (Figure A-2), the test vessel is suspended from the flange of the inner Dewar by means of three thin stainless steel tie-rods. The inner flask is in turn suspended from the micarta cover of the liquid nitrogen vessel. The necessary stainless steel delivery pipes and vacuum lines pass through the flanges by means of Swagelok bulkhead fittings.

The complete cryostat assembly was then surrounded by a sturdy wooden box with Styrofoam filler to support and cushion the glass apparatus. The purpose of this container was primarily to protect personnel from flying glass in the event of glass failure.

Limited visual observation of the contents of the test vessel was afforded by the simple expedient of leaving a 1-inch wide unsilvered strip on opposite sides of each of the Dewar flasks. When these slits were lined up with corresponding slits in the Styrofoam-filled outer box, an explosion-proof spot-light behind the box provided ample illumination of the test vessel.

A thorough search for practical seals through which the agitator shaft could enter the inner Dewar and the test vessel, turned up only one "off-the-shelf" model. Most of the available types were not designed for cryogenic use. The seal selected for use gave a good vacuum tight seal and was reasonably effective at low-positive pressure when properly aligned, but wore unevenly. The seal was not vacuum-tight during stirring.

The schematic diagram of the cryostat (Figure A-3) shows the complete assembly with its associated valves and piping.

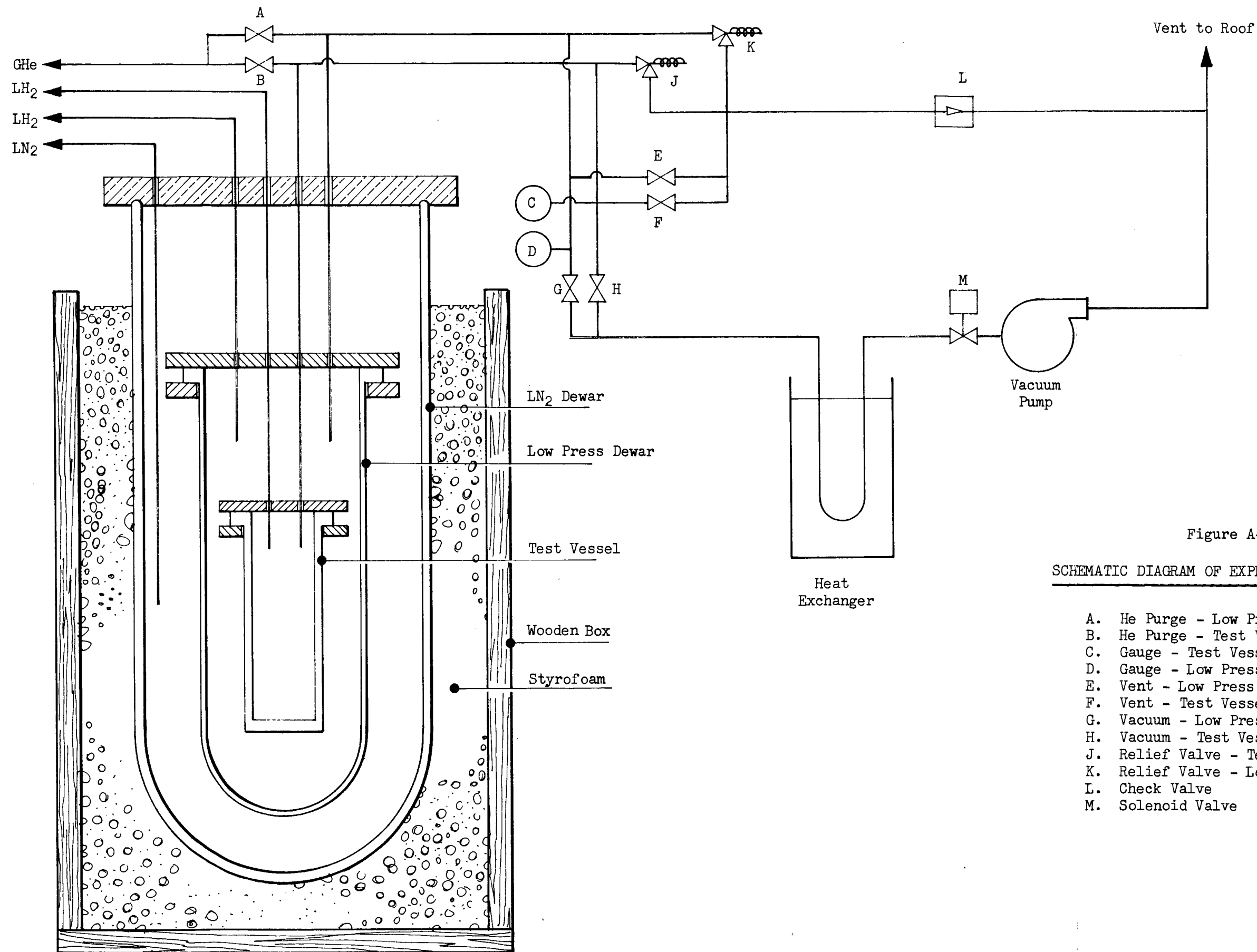


Figure A-3

SCHEMATIC DIAGRAM OF EXPERIMENTAL CRYOSTAT

- A. He Purge - Low Press Dewar
- B. He Purge - Test Vessel
- C. Gauge - Test Vessel
- D. Gauge - Low Press Dewar
- E. Vent - Low Press Dewar
- F. Vent - Test Vessel
- G. Vacuum - Low Press Dewar
- H. Vacuum - Test Vessel
- J. Relief Valve - Test Vessel
- K. Relief Valve - Low Press Dewar
- L. Check Valve
- M. Solenoid Valve

B. Cryostat Checkout With Liquid Hydrogen

The LH₂ Dewar and the inner cryostat vessel were evacuated, purged with helium, and filled with LH₂ to check evaporation rate and the effect of the high-shear mixing device. Evaporation from the inner vessel was quiescent (less than 50 ml per hour) when the mixer was not being operated. Thus the heat path up the stirrer shaft and other connections was quite low.

Mechanical problems of whip in the agitator shaft prevented high-speed operation of the mixer during this trial, but at the maximum speed which was achieved, evaporation from the inner vessel was less than 100 ml per hour. Air sampling with a gaseous hydrogen detector in the vicinity of the rotating shaft seals indicated only minor leakage of hydrogen to the room, and that was mixed with nitrogen from the blanket.

Visibility was satisfactory through the unsilvered slits in the glass Dewars.

The heat leak was so low that the removal of LH₂ at a reasonable rate by evaporation into the vent line required purging with ambient temperature helium.

C. Method of Adding Gellants to LH₂

All of the candidate gellants were outgassed at room temperature (or higher temperature, as stated) at 5 μ Hg pressure to remove adsorbed gases which would be solid at liquid hydrogen temperature, and the vacuum was released with helium (or ultrapure hydrogen) gas. It was expected that traces of adsorbed helium, if any, should be dissolved by the liquid hydrogen. Each gellant was sealed in a polyethylene bag under helium, and positioned just under the cover of the inner cryostat vessel, in such a manner that the bag would be cut open by a knife blade attached to the mixer shaft. In this way, the loss of fluffy gellant by entrainment in vapors during addition of liquid hydrogen was avoided, and the gellant became cooled to liquid hydrogen temperature before addition to the liquid.

When the gellants were added to the liquid hydrogen, there was no rapid boiling or pressure surge, showing that they had been adequately pre-cooled, and there was no large heat release due to wetting by H₂ or adsorption. This technique proved satisfactory and was used, with only minor modifications, for all LH₂ gelling trials.

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